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(71) Applicant (<i>for all designated States except US</i>): BP CHEMICALS LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB).		Published <i>With international search report.</i>	
(72) Inventor; and			
(75) Inventor/Applicant (<i>for US only</i>): SHARP, Christopher [GB/GB]; 12 Aspen Close, Staines, Middlesex TW18 4SW (GB).			
(74) Agent: HAWKINS, David, George; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).			

(54) Title: SUPPORTED POLYMERISATION CATALYST

(57) Abstract

A supported catalyst system suitable for the polymerization of olefins may be prepared by a specific preparative route comprising optionally pretreating a support followed by addition of a neutral metal complex/activator solution. The metal complex may be a metallocene in particular a complex with trifluoromethanesulfonate ligands and the activator is a Lewis Acid.

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SUPPORTED POLYMERISATION CATALYST

The present invention relates to a novel supported polymerisation catalyst composition comprising a discrete metal complex, a support and an activator in particular an activator based on a Lewis acid, to a supported catalyst additionally comprising a Ziegler catalyst component and in particular to a method of preparing said supported catalyst.

5 The use of discrete metal complex based olefin polymerisation catalysts is well-known. Examples of such catalysts include metallocene complexes comprising a bis(cyclopentadienyl) zirconium complex for example bis(cyclopentadienyl) zirconium dichloride or bis(tetramethylcyclopentadienyl) zirconium dichloride disclosed in EP 129368, EP 206794, and EP 260130.

10 In such catalyst systems the discrete metal complex is used in the presence of a suitable activator. The activators most suitably used with such metal complexes are aluminoxanes, most suitably methyl aluminoxane or MAO. Other suitable activators are perfluorinated boron compounds.

15 It would however be beneficial to be able to use simpler and less costly activators with these discrete metal complexes.

20 WO 98/11144 describes catalyst systems based on discrete metal complexes comprising hetero-atom containing chelating ligands together with Lewis acids. Such systems have the advantage of not requiring the use of expensive aluminoxanes as activators. The aforementioned WO 98/11144 discloses that the discrete metal complexes may be supported and may also be used in the presence of Ziegler catalyst components. However there are no teachings of how such supported catalyst systems may be prepared.

25 We have now found that such supported catalyst systems based on discrete metal complexes which are suitable for the polymerisation of olefins and

which do not require aluminoxane activators may be prepared by a specific preparative route which results in the metal complex being predominantly fixed on the support.

- Thus according to the present invention there is provided a method for preparing a supported catalyst composition suitable for the polymerisation of olefins said method comprising the steps of
- (a) optionally pretreating a support,
 - (b) preparing a mixture of a neutral discrete metal complex and activator in a suitable solvent,
 - (c) contacting the support with the mixture from step (b), and
 - (d) removing the solvent to yield a free flowing powder, wherein the metal complex of step (b) has the formula.



where L represents a ligand which remains attached to the metal under polymerisation conditions,

- M is a Group IIIA element or Group IIIB, IVB, VB, VIB or VIII transition metal
- Y is halogen or a group containing at least one O, S, N or P atom bound directly to M
- X may be the same as Y or different and is chosen from halogen, a group containing at least one O, S, N or P atom bound directly to M, hydrogen or hydrocarbyl
- Z is a neutral Lewis base
- n > or = 1
- p > or = 1
- m > or = 0
- q > or = 0.

The support may be for example organic polymer, functionalised organic polymers, polysiloxanes, functionalised polysiloxanes, ion-exchange resins and porous inorganic metal oxides and chlorides for example silica, alumina or magnesium chloride.

The preferred support is silica, in particular dehydrated silica. The inorganic metal oxides and chloride supports may be dehydrated by conventional methods for example by calcination at elevated temperatures. Water may be removed from supports that are unstable to elevated temperatures by Dean

and Stark separation. The dehydrated support material may optionally be pretreated with a Group I-III metal alkyl compound for example by heating in a suitable solvent such as toluene. Particularly preferred compound are those comprising alkyl groups having >2 carbon atoms for example trisiobutylaluminium.

5 The supported catalyst composition according to the present invention may be subsequently treated with an alkylating agent prior to the use as a polymerisation catalyst. A suitable alkylating agent is triisobutylaluminium.

10 It is a particular advantage of the present invention that the catalyst is not dissolved off the support in solvents normally used in polymerisation systems eg. alkanes, aromatics. In this way the metal complex is predominantly fixed to the support.

15 Particularly suitable complexes of the present invention are those having the general formula:



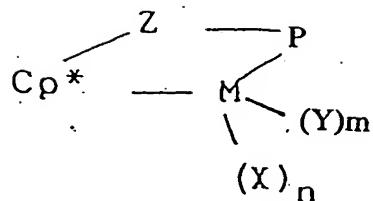
where L represents an unsubstituted or substituted cyclopentadienyl ligand,
 M is a Group IVB, VB, VIB or VIII transition metal
 Y is halogen or a group containing at least one O, S, N or P atom bound directly to M
 X may be the same as Y or different and is chosen from halogen, a group containing at least one O, S, N or P atom bound directly to M, hydrogen or hydrocarbyl
 Z is a neutral Lewis base
 n > or = 1
 p > or = 1
 m > or = 0
 q > or = 0.

25 Suitable metal complexes include metallocene complexes comprising bis(cyclopentadienyl) complexes such as those disclosed for example in EP 129368 or EP 206794.

30 Also suitable for use in the present invention are complexes having constrained geometry such as those disclosed in EP 416815 or EP 420436.

For example complexes having the following general formula may be suitable:

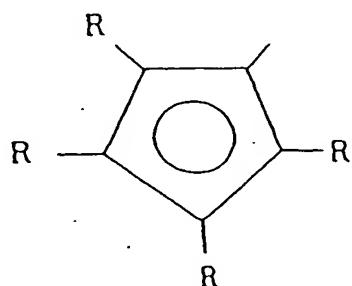
5



wherein:

- 10 Cp^* is a single η^5 -cyclopentadienyl or η^5 -substituted cyclopentadienyl group optionally covalently bonded to M through -Z-P- and corresponding to the formula:

15



- 20 wherein R each occurrence is hydrogen or a moiety selected from halogen, alkyl, aryl, haloalkyl, alkoxy, aryloxy, silyl groups, and combinations thereof of up to 20 non-hydrogen atoms, or two or more R groups together form a fused ring system;

M is zirconium, titanium or hafnium bound in an η^5 bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group and is in a valency state of +3 or +4.

- 25 X each occurrence is hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof (e.g. haloalkyl, haloaryl, halosilyl, alkaryl, aralkyl, silylalkyl, aryloxyaryl, and alkoxyalkyl, amidoalkyl, amidoaryl) having up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms;

30 n and m may be 0, 1 or 2.

Z is a divalent moiety comprising oxygen, boron, or a member of Group IVA of the Periodic Table of the Elements;

- 35 P is a linking group covalently bonded to the metal comprising nitrogen, phosphorus, oxygen or sulfur, or optionally Z and P together form a fused ring

system.

The Y group has the same definition as above.

Illustrative but non-limiting examples of particularly suitable metal complexes for use in the catalyst composition of the present invention are those having the following Y groups in the above general formulae:

- 5 Halide
- Trifluoromethanesulfonate
- Methanesulfonate
- Perchlorate
- 10 Fluorosulfonate
- Nitrate
- Pentafluorotellurate
- Toluenesulfonates including halo substituted
- Benzenesulfonates including halo substituted
- 15 Alkoxides
- Aryloxides
- $\text{HC}(\text{SO}_2\text{CF}_3)_2^-$
- Oxalate and substituted oxalate
- Acetate
- 20 Carboxylate
- Acetylacetone and substituted acetylacetone
- dithioacetylacetone
- Carbamate
- Thiocarboxylate
- 25 Dithiocarboxylate
- Thiocarbamate
- Dithiocarbamate
- Xanthate
- Thioxanthate
- 30 Phosphinate
- Thiophosphinate
- Dithiophosphinate
- dialkyldithiophosphate
- amidinate
- 35 sulphurdiiminate

- amide
tropolonate
oxalate ester
nitrite
5 sulphinate
fluorosulphate
hydroxamate
thiohydroxamate
dithiohydroxamate
- 10 The preferred metal complexes are those in which the Y group is trifluoromethanesulfonate and in which X is the same as Y.
Preferred complexes are those in which M is zirconium, titanium or hafnium.
- 15 Suitable activators for use in the method of the present invention are Lewis acids.
- Examples of suitable Lewis acids are alkyl aluminium compounds eg trimethyl aluminium, triisobutylaluminium, aryl aluminium compounds eg tris(pentafluorophenyl)aluminium, aluminium hydrides eg aluminium trihydride and mixed hydride/aryl/alkyl aluminium compounds eg di-isobutyl aluminium hydride, 20 mono(pentafluorophenyl)di-isobutylaluminium. Also suitable are dialkyl aluminium halides eg dimethyl aluminium chloride or alkyl aluminium dihalides eg methyl aluminium dichloride or ethyl aluminium dichloride.
- Alkyl or aryl borons eg 1,8 naphthalenediylbis(diisobutylborane), boron halides or hydrides, macrocyclic boron compounds eg boracyclododecane, alkyl 25 magnesums or magnesium halides are also suitable. Particularly suitable is tris(pentafluorophenyl) boron.
- Aryloxy aluminium compounds eg (2,7-dimethyl-1,8-biphenylenedioxy)bis(di-iso-butylaluminium) and aryloxy boron compounds eg catecholborane are also suitable.
- 30 Suitable solvents for use in the method of the present invention include alkanes or aromatics. A particularly suitable solvent is toluene.
- The catalyst system according to the present invention may also comprise a second catalyst component in particular a Ziegler catalyst component.
- Thus according to another aspect of the present invention there is provided 35 a method for preparing a supported catalyst suitable for the polymerisation of

olefins comprising:

- (a) impregnating a support with a first catalyst component (A), optionally further treating with a Group I - III metal alkyl compound,
- (b) preparing a mixture of a second catalyst component (B) comprising a metal complex as herein before described and activator in a suitable solvent, and
- (c) contacting the treated support from (a) with the mixture from (b), and
- (d) removing the solvent to yield a free flowing powder.

The polymerisation catalyst component (A) may be a metallocene or may be a Ziegler catalyst component.

10 The Ziegler component of the catalyst composition of the present invention may be any Ziegler catalyst well known in the art but is preferred to be a catalyst comprising essentially atoms of titanium, magnesium and halogen.

15 The present invention also provides a process for the production of polyolefins, in particular homopolymers of ethylene and copolymers of ethylene with minor amounts of at least one C₃ to C₁₀, preferably C₃ to C₈ alpha-olefin. The process comprises contacting the monomer or monomers, optionally in the presence of hydrogen, with a catalyst composition prepared according to the method of the present invention at a temperature and pressure sufficient to initiate the polymerisation reaction.

20 Suitably the alpha olefin may be propylene, butene-1, hexene-1, 4-methyl pentene-1 and octene-1.

25 The olefin polymerisation catalyst compositions prepared according to the present invention may be used to produce polymers using solution polymerisation, slurry polymerisation or gas phase polymerisation techniques. Methods and apparatus for effecting such polymerisation reactions are well known and described in, for example, Encyclopaedia of Polymer Science and Engineering published by John Wiley and Sons, 1987, Volume 7, pages 480 to 488 and 1988, Volume 12, pages 504 to 541. The catalyst according to the present invention can be used in similar amounts and under similar conditions to known olefin polymerisation catalysts.

30 The supported catalyst compositions prepared according to the method of the present invention are particularly suitable for use in the gas phase.

35 The polymerisation may optionally be carried out in the presence of hydrogen. Hydrogen or other suitable chain transfer agents may be used to control the molecular weight of the produced polyolefin.

The present invention will now be further illustrated by reference to the following examples.

Example 1

Preparation of supported catalyst

5 Silica (8g, Crosfield ES70, calcined at 800°C for 5h) was suspended in dry toluene (120ml) and triisobutylaluminium (6ml, 1.0M in toluene) was added. The resulting slurry was then refluxed under a nitrogen atmosphere for 3 hr. at 115-120°C. The solid was recovered by filtration and washed with dry toluene (20ml) and dried on a vacuum line at 20°C.

10 A solution of tris(pentafluorophenyl)boron (50µmol in 7.5ml dry toluene) was added to a solution of bis(1,3-dimethylcyclopentadienyl)zirconium di(trifluoromethanesulfonate) (50µmol in 7.5ml dry toluene) and the mixture shaken for 2 mins. This solution was then added to 1.0g of the pretreated support prepared as above and the solvent removed under vacuum at 20°C, to yield the catalyst as a free flowing powder.

Example 2

Polymerisation

20 The supported catalyst (0.280g) (prepared in example 2) and the treated support material (0.251g) were injected into a stirred gas phase reactor containing dried salt (300g) and triisobutylaluminium (1.7ml, 0.95M in hexane) and to which ethylene was continuously added to maintain a pressure of 8 bar. The polymerisation was carried out at 75°C for 125 min. and 27.1 g. polyethylene was recovered.

Example 3

25 Silica (Crosfield ES 70, dried at 800°C for 5 hr. in flowing nitrogen, 20 kg.) was slurried in dry hexane (110 L) and hexamethyldisilazane (Fluka, 30 mol) added with stirring at 50 °C. Dry hexane (120 L) was added with stirring, the solid allowed to settle, the supernatant liquid removed by decantation and further dry hexane (130L) added with stirring. The hexane washing was repeated a further 30 3 times. Dibutylmagnesium (FMC, 30 mol) was added and stirred for 1 hr. at 50 °C. tert-Butyl chloride (Huls, 60 mol) was added and stirred for 1 hr. at 50 °C. To this slurry was added an equimolar mixture of titanium tetrachloride (Thann & Mulhouse, 3 mol) and titanium tetra-n-propoxide (Thann & Mulhouse, 3 mol) with stirring at 50 °C for 2 hr. followed by 5 washings with dry hexane (130L). The 35 slurry was dried under a flowing nitrogen stream to give a solid, silica supported

Ziegler catalyst.

Example 4

- A solution of tris(pentafluorophenyl)boron (50 µmol in 7.5 ml. dry toluene) was added to a solution of bis(1,3-dimethylcyclopentadienyl)zirconium 5 trifluoromethane sulfonate (50 µmol in 7.5 ml. dry toluene) and the mixture shaken for 2 mins. This solution was then added to 1.0g. of the silica supported Ziegler catalyst prepared in example 3 and the solvent removed under vacuum at 20 °C, to yield the catalyst as a free flowing powder.

Example 5

10 Polymerisation

- A 3 litre reactor equipped with a helical stirrer was heated to 95 °C for 1.5 hr. under flowing nitrogen. The temperature was reduced to 45°C and dry sodium chloride (300 g) was then added with trimethylaluminium (TMA) solution (2 ml of 2M TMA in hexane) and the reactor heated at 85°C for 2 hr. The reactor was 15 purged with nitrogen, cooled to 45°C and triisobutylaluminium (TiBA) solution (10 ml of 0.14M TiBA in hexane) added. The temperature was raised to 75°C and hydrogen (0.06 bar) and 1-hexene (1.2 ml) added prior to the addition of ethylene (8.0 bar). Reaction was started by injection of the metallocene modified Ziegler catalyst (0.21g) and TiBA/silica scavenger* (0.13g) into the reactor. The 20 temperature was maintained at 75°C and ethylene added to maintain constant pressure. The gas phase was monitored by mass spectrometer and hydrogen and 1-hexene were added as necessary to maintain constant gas phase concentrations. The polymerisation was carried out for 90 min. and 97 g of polyethylene with a polydispersity of 6.4 was recovered.

25 Scavenger material*

- Silica (8g, Crosfield ES70, calcined at 800°C for 5 hr) was suspended in dry toluene (120 ml) and triisobutylaluminium (6 ml, 1.0M in toluene) was added. The resultant slurry was then refluxed under a nitrogen atmosphere for 3 hr. at 115-120°C. The solid was recovered by filtration and washed with dry toluene (20 ml) and dried on a vacuum line at 20°C.

Claims:

1. A method for preparing a supported catalyst composition suitable for the polymerisation of olefins comprising the steps of:

- (a) optionally pretreating a support,
- (b) preparing a mixture of a neutral discrete metal complex and activator in a suitable solvent,
- (c) contacting the support with the mixture from step (b), and
- (d) removing the solvent to yield a free flowing powder, wherein the metal complex of step (b) has the formula.



10 where L represents a ligand which remains attached to the metal under polymerisation conditions,

M is a Group IIIA element or Group IIIB, IVB, VB, VIB or VIII transition metal.

Y is halogen or a group containing at least one O, S, N or P atom bound directly to M

15 X may be the same as Y or different and is chosen from halogen, a group containing at least one O, S, N or P atom bound directly to M, hydrogen or hydrocarbyl

Z is a neutral Lewis base

20 n > or = 1

p > or = 1

m > or = 0

q > or = 0.

25 2. A method according to claim 1 wherein the complex has the general formula:



- where L represents an unsubstituted or substituted cyclopentadienyl ligand,
- M is a Group IVB, VB, VIB or VIII transition metal
- Y is halogen or a group containing at least one O, S, N or P atom bound directly to M
- X may be the same as Y or different and is chosen from halogen, a group containing at least one O, S, N or P atom bound directly to M, hydrogen or hydrocarbyl
- Z is a neutral Lewis base
- n > or = 1
- p > or = 1
- m > or = 0
- q > or = 0.
3. A method according to either of claims 1 or 2 wherein
- 15 Y is trifluoromethane sulfonate,
X = Y and M is zirconium.
4. A method according to any of the proceeding claims wherein the support is silica.
5. A method according to claim 4 wherein the support is pretreated with a
- 20 Group I-III metal alkyl.
6. A method according to any of the preceding claims wherein the activator is a Lewis acid.
7. A method according to claim 6 wherein the Lewis acid is tris(pentafluorophenyl) boron.
- 25 8. A method for preparing a supported catalyst suitable for the polymerisation of olefins comprising:
- (a) impregnating a support with a first catalyst component (A), optionally further treating with a Group I - III metal alkyl compound,
 - (b) preparing a mixture of a second catalyst component (B) comprising a metal
- 30 complex as herein before described and activator in a suitable solvent, and
- (c) contacting the treated support from (a) with the mixture from (b), and
 - (d) removing the solvent to yield a free flowing powder.
9. A method according to claim 8 wherein the first catalyst component (A) is a Ziegler catalyst.
- 35 10. A method according to claim 9 wherein the Ziegler catalyst comprises

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essentially the atoms of titanium, magnesium or halogen.

11. A process for the polymerisation of ethylene or the copolymerisation of ethylene and C₃-C₁₀ alpha olefins comprising carrying out the process in the presence of a supported catalyst system as prepared according to claims 1-10.

5 12. A process according to claim 11 carried out in the gas phase.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F4/60 C08F10/02

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 589 638 A (MITSUBISHI PETROCHEMICAL CO) 30 March 1994	1-4,11,
Y	see example 7	12
Y	see column 3, line 17 - line 31	6,7
	see column 16, line 1 - line 29	6,7
P,X	WO 97 31035 A (EXXON CHEMICAL PATENTS INC) 28 August 1997	1-4,8
	see example 1	---
X	WO 96 35729 A (FINA RESEARCH ; RAZAVI ABBAS (BE); DEBRAS GUY (BE)) 14 November 1996	1-4
	see example 1	---
	see claims 1,13	---
X	US 5 032 562 A (LO FREDERICK Y ET AL) 16 July 1991	8-12
	see examples 1,3,4	---
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 13871 A (MOBIL OIL CORP) 26 May 1995 see examples 1,2,4 -----	8-12
X	EP 0 591 756 A (IDEMITSU KOSAN CO) 13 April 1994 see example 24 -----	1-4,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internatinal Application No

PCT/GB 98/01961

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0589638 A	30-03-1994	JP 6100622 A		12-04-1994
		DE 69304004 D		19-09-1996
		DE 69304004 T		23-01-1997
		US 5474962 A		12-12-1995
WO 9731035 A	28-08-1997	AU 2054897 A		10-09-1997
		WO 9731040 A		28-08-1997
WO 9635729 A	14-11-1996	EP 0830395 A		25-03-1998
US 5032562 A	16-07-1991	CA 2042961 A		22-11-1992
		EP 0514594 A		25-11-1992
		JP 5105718 A		27-04-1993
WO 9513871 A	26-05-1995	AU 687943 B		05-03-1998
		AU 1097295 A		06-06-1995
		CA 2174660 A		26-05-1995
		CN 1136286 A		20-11-1996
		EP 0729387 A		04-09-1996
		JP 9505236 T		27-05-1997
		SG 43850 A		14-11-1997
		US 5614456 A		25-03-1997
		ZA 9408934 A		10-05-1996
EP 0591756 A	13-04-1994	JP 6316605 A		15-11-1994
		US 5461127 A		24-10-1995